

Study of Schiff's bases as surface modifiers for corrosion protection of copper in sulphuric acid

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Received 14 February 2006; revised received 19 July 2006; accepted 6 September 2006

Surface modification of copper by newly synthesised Schiff's bases, *N*-[(1*E*)-2-furylmethylene]-*N*-phenylamine (FA), 3-[[[(1*E*)-2-furylmethylene] amino] phenol (FAP), 4-[[[(1*E*)-2-furylmethylene] amino] benzoic acid (FAB) and 2-[(*E*)-[(3-hydroxyphenyl) imino] methyl] phenol (SAP), in 0.5 M sulphuric acid solution was investigated. The corrosion behavior of surface treated copper specimens was tested by galvanostatic polarization technique. The effect of concentration of Schiff's bases in the treatment bath, treatment time and temperature of the corrosive medium on the corrosion protection efficiency of Schiff's bases was investigated. Among the compounds studied, the protective film formed by FAB showed maximum protection efficiency. The inhibitive action of Schiff's bases was due to their adsorption and consequent growth of the protective film on the metal surface. The inhibitive effectiveness depended strongly on the molecular structure of the Schiff's base. The interaction of the compounds with the metal surface was confirmed by FTIR technique. The SEM studies showed the modification of copper surface due to the adsorption of Schiff's bases.

Keywords: Schiff base, Surface modifier, Copper corrosion, Sulphuric acid

IPC Code: C07C251/00, C23F11/00

Copper is most commonly used material in heating and cooling systems because of its excellent thermal conductivity and good mechanical workability. However, the efficiency of the equipment is decreased due to the formation of scale and corrosion products on the surface. Therefore a periodic cleaning the surface is necessary which can be done by using pickling agents such as sulphuric acid and hydrochloric acids. These pickling agents not only attack the scale of corrosion products but also the metal surface. The undesirable destruction of metal surface can effectively be reduced by adding an effective corrosion inhibitor to the pickling solution.

Commonly used inhibitors for copper corrosion are toxic compounds that should be replaced with the new eco-friendly inhibitors. Most of the inhibitors are derivatives of benzotriazole¹, thiazole², imidazole³ etc. It is established that the lone pair of electrons on nitrogen and the protonation property of the azo and thiol groups are responsible for the formation of protective film on the metal surface and hence control the corrosion. The nature and stability of the film depends upon the molecular structure and geometry of the inhibitor. Diazonium salts form covalent bond with copper through its nitrogen⁴. Schiff's bases are used as corrosion inhibitors in various corrosive

media⁵ for metals like zinc and iron. Schiff's bases have been found to exhibit greater corrosion protection efficiency better than the corresponding aldehydes and amines⁶. The imine compounds are found to be suitable surface modifiers for the metals⁷.

The present paper focuses on the use of Schiff's bases of furfural and salicylaldehyde with different substituted anilines, for surface treatment of copper against corrosion in sulphuric acid medium. The used compounds consist heterocyclic ring and an imine group with different substituents. The surface of copper was modified by immersion method. The influence of concentration of inhibitors was studied by electrochemical methods.

Experimental Procedure

All the chemicals used were of AR grade (s. d. fine chemicals, Mumbai, India). The Schiff's bases, *N*-[(1*E*)-2-furylmethylene]-*N*-phenylamine (FA), 3-[[[(1*E*)-2-furylmethylene] amino]phenol (FAP), 4-[[[(1*E*)-2-furylmethylene] amino]benzoic acid (FAB) and 2-[(*E*)-[(3-hydroxyphenyl) imino] methyl] phenol (SAP), were prepared by adopting standard procedures⁸. The compounds were separated, recrystallised and the purity was confirmed by thin layer chromatography. The formation of the Schiff's

bases was confirmed by FTIR spectroscopy (Shimadzu-FTIR-8400S). The structures of the compounds are shown in Fig. 1.

The copper metal used for the corrosion experiments had a purity of 99.99%. The copper plates with dimensions $1 \times 6 \text{ cm}^2$ were selected. The exposed surface area of the copper was 1 cm^2 . The remaining portion of the metal was covered with araldite. The electrode surface was abraded with emery paper (200-1000 grit size) and degreased with ethanol. For surface treatment of copper metal, the solutions of Schiff's bases of different concentrations (1- 10% *w/v*) in ethanol were used. Copper strips were immersed in the inhibitor solutions for different time intervals. The surface treated copper specimens were washed with distilled water, dried in hot air and used as working electrodes.

A conventional three-compartment cell, with surface treated copper plate as working electrode, saturated calomel (SCE) as reference electrode and platinum as counter electrode was used for the polarization studies using a potentiostat/galvanostat (model: Elico CL 95). Anodic and cathodic

polarization potentials were recorded in the current density range of 0.1 to $500 \mu\text{A}/\text{cm}^2$. The potentials were scanned primarily in the cathodic direction from corrosion potential and then subsequently in the anodic direction. The electrode was held in the test solution for few seconds, prior to the measurements, to ensure reliable corrosion potential. Polarization studies were also carried out at 298, 308, 318, 328 and 338 K in the same method as explained above by using a thermostat (model: PaaCaa, Raaga Industries, Chennai, India). The cell was kept for 30 min in the thermostat to attain desired temperature before the experiments. The corrosion parameters were obtained from the plot of E versus $\log J$. The E_{corr} and J_{corr} values were calculated from the Tafel plots.

FTIR spectra of the prepared compounds and the compounds scrapped from the metal surface were taken. The surface morphology of the unmodified and surface modified copper specimens after anodic polarization were studied by SEM technique (model: JEOL, JSM 6400).

Results and Discussion

The anodic and cathodic polarization curves in sulphuric acid medium for FA treated copper surface are shown in Fig. 2. The effect of inhibitor concentration on the modification of copper surface against corrosion in sulphuric acid medium is given in Table 1. The results showed that, with increase in the concentration of FA, inhibition efficiency is increased and reaches a maximum value at a concentration of 8%. Above this concentration the inhibition efficiency almost remains constant. Thus the optimum concentration of FA was fixed at 8%. The corrosion potential is shifted from -85 to -160 mV . This shows that there is a small domination in the inhibition of

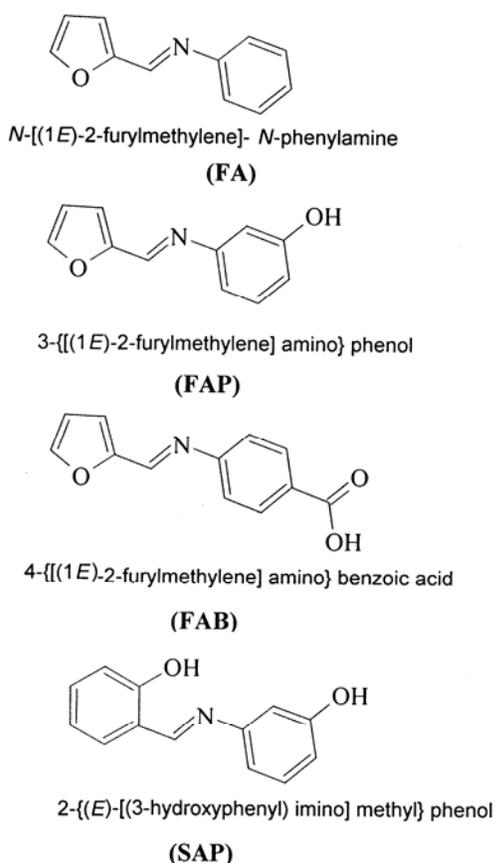


Fig. 1 — Structure of Schiff's bases, (a) FA, (b) FAP, (c) FAB and (d) SAP.

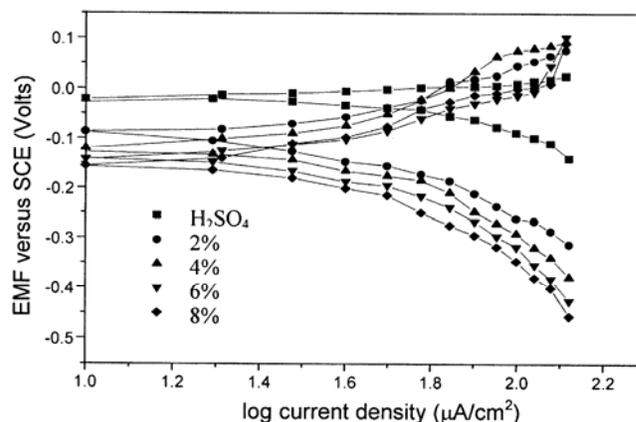


Fig. 2 — Anodic and cathodic polarization curves in sulphuric acid for copper surface treated with FA.

Table 1 — Galvanostatic polarization values in 0.5 M H₂SO₄ for copper treated with FA at 298K.

Schiff's base	Concentration (%)	E_{corr} (mV)	b_c (mVdec ⁻¹)	$-b_a$ (mVdec ⁻¹)	J_{corr} ($\mu\text{A}/\text{cm}^2$)	z (%)
FA	2	-85	575	175	73.8	46
	4	-125	398	97	43.5	66
	6	-145	354	73	38.3	70
	8	-160	288	67	23.8	81
FAP	2	-60	178.3	75.10	56.32	58
	4	-90	153.2	64.5	43.52	66
	6	-130	125.1	52.6	30.70	76
	8	-180	121.3	48.8	20.48	84
FAB	2	-20.0	163.1	54.5	63.10	50
	4	-12.5	173.4	67.4	41.70	63
	6	+17.5	152.2	43.9	26.90	88
	8	+25.0	159.0	52.1	19.95	91
SAP	2	-11.0	190.4	81.3	70	41
	4	+50.0	174.0	74.1	50	66
	6	+55.0	158.8	66.6	37	71
	8	+65.0	154.3	63.5	25	86

cathodic reaction. Thus FA influences the cathodic reaction and hence it is a good cathodic surface modifier.

For FAP the corrosion potential values shifted towards more negative values with the increasing concentration of the compound in the treatment bath. This means that there is a small domination in the inhibition of the cathodic reaction. The decrease in the corrosion rate can be seen from the decrease in the corrosion current values⁹. Figure 3 shows the polarization curves in sulphuric acid medium for the treated copper surface with FAP. It shows large deviation of the potential values on both anodic and cathodic sides when compared to the curves corresponding to the values obtained with untreated metal. The corrosion protection efficiency of the compound increased with increase in the concentration of the compound in treatment bath. The optimum concentration for FAP was same as that of FA. The shift in E_{corr} values in the case of FAP were from -60 to -180 mV and the shift was towards cathodic direction. This revealed that the FAP blocks the cathodic sites and reduces the rate of cathodic reaction. Thus FAP also acts as cathodic inhibitor for copper in sulphuric acid medium.

Figure 4 shows the variation of corrosion inhibition efficiency of treated specimens with the concentrations of FAB. The shift in the E_{corr} values from -20 to +25 mV shows that FAB is a good anodic inhibitor. Figure 5 represents the polarization curves

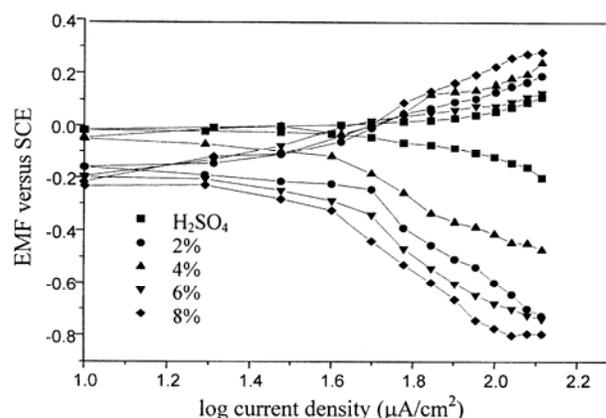


Fig. 3 — Anodic and cathodic polarization curves in sulphuric acid for copper surface treated with FAP.

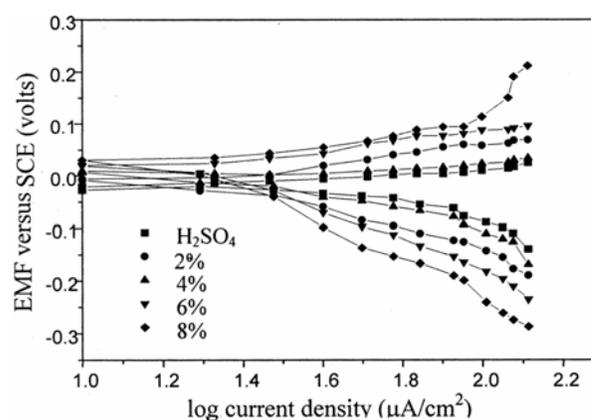


Fig. 4 — Anodic and cathodic polarization curves in sulphuric acid for copper surface treated with FAB.

in sulphuric acid medium for the treated copper specimens with SAP. The shift in the E_{corr} values was towards anodic direction and hence it acts as a good anodic inhibitor. Table 1 shows the variation of corrosion inhibition efficiency of treated copper specimens with the concentration of SAP. This shows the lower rate of oxidation of metal by the treatment with SAP¹⁰.

The optimum concentration was 8% for all the Schiff's bases. The protection efficiency rendered by

the present molecules to the copper surface can be judged by performing polarization studies at different temperatures. Figure 6 shows the anodic and cathodic polarization curves in sulphuric acid at different temperatures for the copper specimens treated with optimum concentration of FAP. From the corrosion parameters given in the Table 2, it is revealed that the increase in corrosion current with temperature shows that there is an acceleration in the rate of dissolution of metal. From this observation it can be inferred that

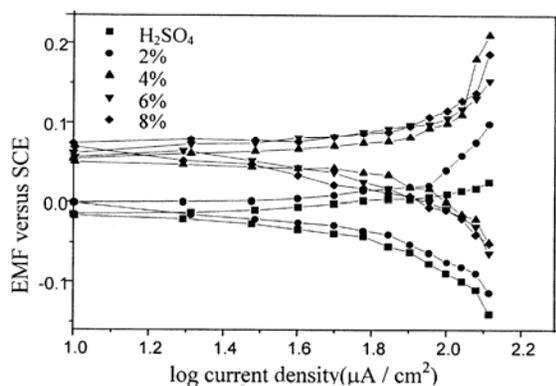


Fig. 5 — Anodic and cathodic polarization curves in sulphuric acid for copper surface treated with SAP.

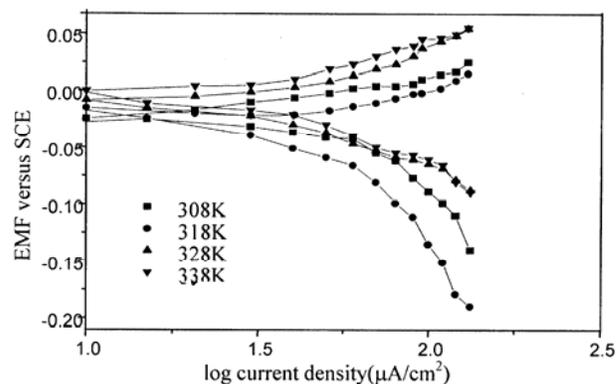


Fig. 6 — Anodic and cathodic polarization curves in sulphuric acid at different temperatures for copper treated with optimum concentration of FAP.

Table 2 — Corrosion parameters in 0.5 M sulphuric acid at different temperature, for surface treated and untreated copper specimens by the Schiff's bases, obtained by the Tafel extrapolation method.

Solution	E_{corr} (mV)	$-b_c$ (mVdec ⁻¹)	b_a (mVdec ⁻¹)	J_{corr} ($\mu\text{A}/\text{cm}^{-2}$)	z (%)
Temperature= 308K					
0.5 M H ₂ SO ₄	-10	775.6	89.1	79.43	-
FA	-30	431.1	68.3	28.12	64
FAP	-15	501.3	71.1	19.2	76
FAB	+10	165.2	65.4	6.6	92
SAP	+20	149.3	47.1	8.06	89
Temperature= 318K					
0.5 M H ₂ SO ₄	-20	467.2	57.1	97.21	-
FA	-24	320.5	69.2	30.41	66
FAP	-17	581.1	74.0	27.20	70
FAB	+09	351.3	56.4	8.10	91
SAP	+03	270.5	69.5	9.10	89
Temperature= 328K					
0.5 M H ₂ SO ₄	-10	535.3	59.0	113.3	-
FA	-30	602.5	63.2	46.60	59
FAP	-20	412.1	41.5	37.40	66
FAB	+12	341.2	39.2	10.30	90
SAP	+01	290.0	44.0	14.41	86
Temperature= 338K					
0.5 M H ₂ SO ₄	-05	670.4	69.4	191.5	-
FA	-26	230.2	81.1	88.6	53
FAP	-20	184.2	50.3	67.3	64
FAB	+10	243.3	83.6	21.2	88
SAP	+02	310.1	85.1	41.8	78

the protection film formed by the molecules get damaged at higher temperature. This in turn causes the exposure of metal surface to the corrosive environment and hence a decrease in the protection efficiency. It was noticed that the temperature had the greater influence on the specimens treated with FAP. The increase in temperature may affect the rate of adsorption/desorption and if the corrosion rate is faster than the rate of adsorption, there may be a decrease in the corrosion protection efficiency¹¹.

The immersion time for the modification of surfaces was 2 h for all the treatment baths. In order to know the effect of immersion time on the protection efficiency, the experiments were conducted by varying the immersion time from 2 to 10 h (2, 4, 6, 8 and 10 h). In all these experiments the concentration of the compounds in the treatment bath were at their optimum value. The protection efficiency calculated based on the values of J_{corr} revealed that FA, FAP and FAB gave same efficiency irrespective of immersion time while SAP showed gradual increase in protection efficiency with immersion time.

For the corrosion of metal the anodic sites are responsible and the dissolution of metal as metal ions takes place through these anodic sites. More the number of anodic sites on the metal the higher is its corrosion rate. Also the cathodic sites assist the anodic reaction and thus indirectly are responsible for corrosion¹². In the present study FA and FAP act as good cathodic inhibitors. This suggested that these molecules block the cathodic sites for the cathodic reaction. As a result the rate of cathodic reaction is reduced and this brings down the rate of metal dissolution. The compounds FAB and SAP act as anodic inhibitors and thus these molecules directly block the anodic sites and hence reduce the corrosion rate. The inhibitive action is mainly due to the adsorption of molecules on metal surface¹³.

The corrosion protection ability of the investigated Schiff's bases may be due to the chemical interaction with active sites of copper. The active functional groups present in the Schiff's base can form complexes with many metals¹⁴. Thus, the Schiff's bases can chemically interact with the metal to form a

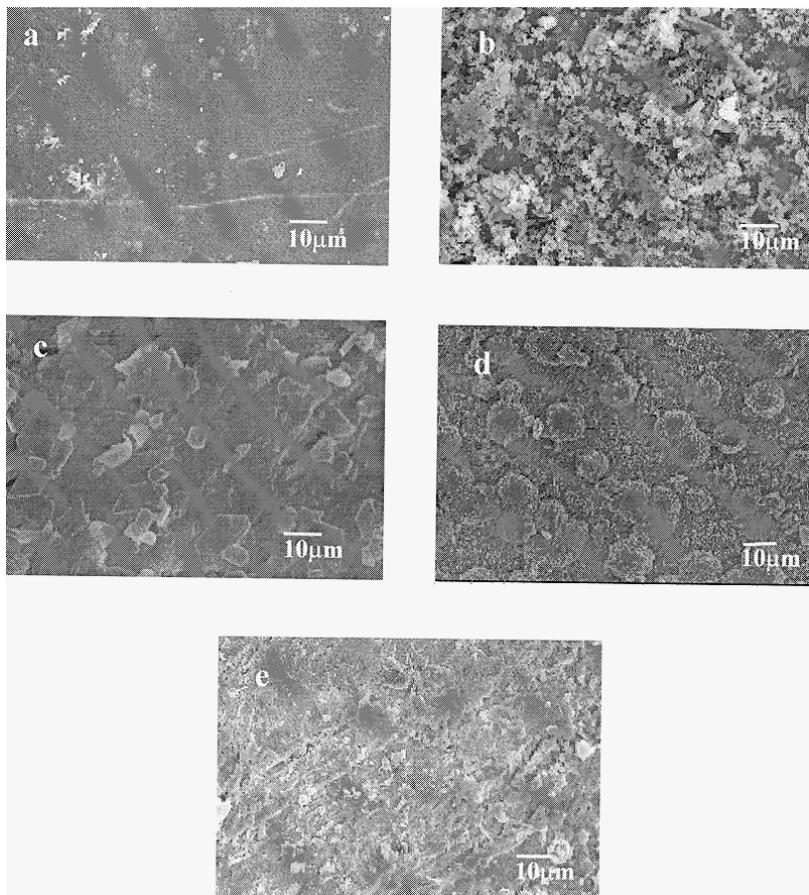


Fig. 7 — Scanning Electron Micrographs of anodically polarized copper surface treated and untreated with Schiff's bases (a) Untreated copper surface, (b) treated by FA, (c) treated by SAP, (d) treated by FAB, (e) treated by FAP.

protective film that can decrease the corrosion rate of metal. The presence of electron donating functional groups in the compound can increase the electron density on the $>C=N-$ group of the Schiff's bases¹⁵. The synthesized molecule contains $>C=N-$ groups in order to form a complex with copper and aromatic ring oriented to the environment protects the copper surface against corrosion.

FTIR spectra of the synthesized compounds and the compounds scrapped from the copper metal surface were taken. The stretching frequencies corresponding to $>C=N-$ group in FA, FAP, FAB and SAP were found to be shifted to lower frequencies upon complexation with surface atoms of metal. The shift was from 1641.12 to \sim 1620, 1632 to \sim 1612, 1650 to \sim 1630 and 1654.8 to \sim 1643 cm^{-1} for FA, FAP, FAB and SAP, respectively. This confirms that there is an interaction of the $>C=N-$ group of the inhibitors with the metal atoms¹³.

SEM studies

Figure 7a shows the SEM image of untreated copper taken after anodic polarization. This shows number of spots covered with corrosion products due to the localized attack of the corrosive medium. Figure 7b, c, d and e correspond to the images of copper specimens treated with FA, SAP, FAB and FAP, respectively, taken after anodic polarization. In case of surface treated samples no pits or corrosion products were observed. This is because of the presence of protective film on the surface.

Conclusion

All the four synthesized Schiff's bases have shown good inhibiting property for copper corrosion in sulphuric acid medium. The inhibition efficiency is in the order of 81, 84, 86, and 91% for FA, FAP, SAP

and FAB, respectively. The inhibitive action of the inhibitors may be due to the chemisorption reaction between the imine group and metal atoms of the surface. The corrosion protection efficiency was found to vary in accordance with the functional groups present in the Schiff's bases. These compounds can be used for corrosion protection of copper even in appreciable concentration of sulphuric acid.

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